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M. Kay

RALA SEMI WORKS DEVELOPMENT (1949 *)

ION EXCHANGE STUDY

INV. 64

This document has been approved for release
to the public by:

David R Hamrin 3/10/95
Technical Information Officer Date
ORNL Site

[redacted]

[redacted]

FLS-189	– Decl.	Barium 140 Separation Development in the Semi-Works. Period 8/10/49 - 11/10/49.
FLS-218	– Decl.	Barium^{140} Development in the Semi-Works. Period 12/10/49 - 1/10/49.
FLS-242	– Decl.	Barium^{140} Separation Development in the Semi-Works. Period 11/10/49 - 2/10/50.
FLS-275	– Decl.	Barium Separation and Purification - Unit Operations. Period 2/10/50 - 3/10/50.
FLS-311	– Decl.	Barium Separation and Purification - Unit Operations.
FLS-340	– Decl.	RaLa Process - Unit Operations, Part I Ion Exchange Development. Period 2/10/50 - 5/10/50.
FLS-414	– Decl.	RaLa Process - Unit Operations, Part I Ion Exchange Development. Period 6/10/50 - 7/14/50.
FLS-375	– Decl.	RaLa Process - Unit Operations, Part I - Ion Exchange Development. Period 5/10/50 - 6/10/50.
FLS-378	– Decl.	Sr^{90} Extraction and Partial Purification in the Unit Operations RaLa Development.

[redacted]

FLS-189
Technical Division
Chemical Technology Department

To: F. L. Steahly

Date: November 2, 1949

From: I. R. Higgins

Report Period: Aug. 10 to Nov. 10, 1949

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Problem No. TDSI-34

Part

QUARTERLY REPORT

Title: Barium 140 Separation Development in the Semi-Works

Work by: I. R. Higgins, R. H. Vaughan, W. A. Horne, J. B. Goodman, D. B. Masters, and W. E. Shockley

Secret Notebook No.

INTRODUCTION

The present process for the production of Ba 140 consists of precipitation of the barium from dissolved slug solution as sulfate using lead carrier, metathesis of the lead-barium sulfates to carbonates using potassium carbonate, solution of the carbonate precipitates in nitric acid, electrolysis of the lead as PbO_2, evaporation of the barium nitrate to dryness, solution of the barium nitrate in water and precipitation again in hydrochloric acid-ether to extract, and final concentration of the barium chloride. All the barium-lead sulfate and carbonate separations are made by decantation and losses are often high because of mechanical loss of precipitate. Development work using both a filter and centrifuge is being carried on on a semi-works scale to reduce these mechanical losses. A full-scale ion exchange column is being run to replace the electrolysis step for lead and the ether-hydrochloric acid stripping of strontium.

SUMMARY:

Filtration rather than centrifugation has been favored for the 706-D equipment change over for reducing mechanical losses of lead-barium sulfate and carbonate precipitates which are now separated by decantation. Either a filter or a centrifuge reduces the losses sufficiently, but a filter is less expensive to install and is less subject to mechanical failure. Considerable difficulty was encountered with filter plugging. Y-12 UNH which contained graphite was the cause of plugging. To circumvent this trouble, "cold" Hanford slugs were dissolved for UNH which are the barium source for production, but even quicker plugging was observed with virtual stoppage of the flow. The difficulty was traced to silicon or silica particles from the Al-Si alloy bonding agent used in Hanford slugs. Efforts to dissolve chemically or flush off mechanically the silicon residue which adheres after jacket removal were unsuccessful. Prefiltration of Hanford slug derived UNH using filter aid in recent runs prevented filter plugging in the precipitation steps. A 6" precoated "G" micro-metallic filter was used with 5 grams per liter of "Cellite" 545 filter aid. Crud containing UNH was filtered at a rate of 0.5-1.2 liters per minute. The subsequent lead-barium sulfate precipitate filtered satisfactorily at a rate of 1 to 2.5 liters per minute through a 6 inch "G" filter. Final demonstration runs now underway will employ prefiltration.

Barium losses remain around 1% or less. Metathesis has been complete since product solutions are not cloudy. Twelve to fifteen hours are required for the complete process, counting from the 1st precipitation, until the metathesis cake is dissolved. Ion exchange runs have lagged because of filter trouble and too small a resin bed for the quantity of lead to be separated.

From the most recent runs from which analytical results have been obtained, barium yields of approximately 100% and losses of 0.1% to 0.2% have been demonstrated, with lead-reduced from 87 grams to 0.02 grams in the product, strontium decontaminated by a factor of 100 to 4300, and sodium reduced to 3.3 grams, on one run, based on full scale.

Iron removal has been demonstrated to be efficient but corrosion of equipment has also occurred. About 30 hours are required for a full scale ion exchange cycle.

50-1-193 5

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FLS-218
Chemical Technology Dept.
Technical Division

To: F. L. Steahly

Date: January 9, 1950

From: I. R. Higgins

Report Period: 12-10-49 - 1-10-50

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Problem No. TDSI-34

MONTHLY REPORT

Title: Barium 140 Development in the Semi-Works

Work by: I. R. Higgins, R. H. Vaughan, W. A. Horne, J. B. Goodman, D. B. Masters, and W. E. Shockley

SUMMARY

A report is in progress on mechanical separation of lead-barium precipitates byrfiltration and centrifugation and the acetate-citrate ion exchange purification process. Filter and ion exchange equipment is being designed for the final production equipment. The week of January 15 a full activity level ion exchange run will be run with the acetate citrate process to determine radiation effect on the process operation, if any. Semi-Works development is being continued on a Versene ion exchange process for elimination of the metathesis step. Results indicate that this method of operation is very satisfactory.

#1351

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Table I

Purification of Ba^{140} by Versene Solution of Pb-Ba Sulfate Precipitate and a Two Ion Exchange Column System

A. MS* Column 4" x 2" Dowex 50, Na form, 60-100 Mesh

B. Purification Column 3" x 7" Dowex 50, Na form, 60-100 Mesh

Feed - 87 grams lead
about 0.1 grams iron
1.2 - 1.7 curies Ba
0.7 - 1.9 curies Sr
42 grams Na on Purification Column

Eluting Solution	Column	Percent				Total Grams					
		Barium		Strontium		Iron		Lead		Sodium	
		32	33	32	33	32	33	32	33	32	33
Feed Waste	MS	0.06	0.13	205	25	0.088	0.11	81.5	77.0		
Crude Product	MS	143	99.5	160	92.5	0.012	0.012	<0.047	1.67		
Cleanup	MS	5.2	17.9	—	—						
Feed Waste	Puri-	0.005	0.05	0.23	0.08	0.128	0.111	< 0.11	< 0.13		
Sr Waste	Puri-	0.002	0.006	23.8	66.9	—	<0.01	1.03	< 0.08		
Na Waste	Puri-	0.001	0.01	76.0	2.3						
Ba Product	Puri-	74.0	84.5	10.7	0.29	0.146	0.069	<0.025	<0.037	2.4	364
Clean-up	Puri-	0.24	—								

*MS - Metathesis Substitute

From the Table it will be noted that the only high barium loss (although not shown by the crude product analysis) is in the MS column clean-up. In future runs more Versene will be used at a slower flow rate to more completely elute the barium. The final yields are less than 100% possibly because of loss in mechanical transfer from the waste to feed tank. In Run 32 the strontium eluting solution was cut off too quickly which accounts for the high strontium in the product. The iron removal steps indicate all the iron has been removed but more iron appears in the product because of nitric acid corrosion of stainless steel. The bulk of the lead is removed in the first column. Too little sodium eluting solution has been used in several runs because the spectrographic analysis of the product indicated no sodium. Late ionic analysis indicate 2 or 3 grams which can be removed with more HCl.

50-2-173 8

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FLS-242
Chemical Technology Division

To: F. L. Steahly

Date: February 10, 1950

From: I. R. Higgins

Report Period: 11/10/49-2/10/50

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Problem No. TDSI-34

Decl.

QUARTERLY REPORT

Title: Barium 140 Separation Development in the Semi-Works

Work by: I. R. Higgins, J. B. Goodman, D. B. Masters, and W. E. Shockley

SUMMARY

A progress report is nearly complete on the lead-barium precipitate separations by centrifugation and filtration and the acetate-citrate ion exchange process. Ion exchange runs have been made with about 3000 curies of active barium with no noticeable effect of this amount of radiation on the operation of a 3" x 7" Dowex 50 resin bed. Development is continuing on Versene ion exchange procedures and centrifugation of barium sulfate without lead carrier.

At the present stage of development, it has been decided to design for a crud filter, using filter aid, a lead-barium precipitate filter, and a 3" x 7" one column ion exchange process using the "Metathesis-Versene"procedure. The crud filter is necessary to remove siliceous filter plugging material derived from the jacket bonding agent. Using a precoated "G" micrometallic filter and 5 g/l of Celite 545 filter aid, 100 gallons can be filtered in about one hour on a one square foot filter. Development is being carried on to dissolve or loosen the crud from the slugs in order to eliminate the crud filter. The crud is loosened, after jacket removal, by alternate

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treatment of 6M NaOH with peroxide and 1M HNO_3. Three caustic-acid treatments have removed all visible black crud from 4-8" Hanford slugs in the Semi-Works dissolver. The final UNH solution filtered very rapidly up to 90 gallons per square foot of "G" micrometallic filter area, but was almost completely plugged at 100 gallons. This is operating very close to the desired conditions. Crud removal is slow and not entirely predictable as yet. Future runs are planned with vigorous agitation with emery powder slurry in hopes of cleaning the slugs more rapidly. If filter plugging does occur, however, it is very rapidly unplugged with 0.01 M hydrofluoric acid. Any filter installation should be designed for washing. The Semi-Works process "G" filter has been washed with 0.01 M hydrofluoric acid between each run 6 times without noticeable increase in barium loss.

The process filter for the lead-barium sulfate and carbonate precipitates need only be half the area of the crud filter, if the crud filter is used, to give the same flow rate of 100 gallons per hour. Barium losses using the "G" filter remain well below 1%.

Because the Semi-Works precipitator is cylinderical and the 706-D precipitator is conical, the volume of metathesizing solution used in the Semi-Works had to be increased over that specified by the standard procedure so the agitator would hit the liquid. The 706-D operations metathesize 3 times in 5 liters of 3 M K_2CO_3. The Semi-Works at 1/2 scale metathesizes 2 times in 5 liters of 4 M K_2CO_3. From the sulfate analysis from 5 runs, the Semi-Works metathesis was 97% to 99% complete. After a filter is installed in the 706-D equipment, it is recommended that a more volume of stronger metathesizing solution be used since no decantation problem is involved.

Ion Exchange Purification

A memo has been written reporting the results of the operation of ion exchange separation of kilocuries of activity. No observable radiation effects were noted in processing 3000 curies of barium and a total of 6000 curies on a 3" x 7" Dowex 50 resin bed. In the Semi-Works on full volume scale and about one curie of barium activity with the "Acetate-Citrate", "Metathesis-Versene", and the "2 Column No Metathesis-Versene" processes, barium losses have been demonstrated below 1%, lead has been below the polorograph detectible limits, sodium less than 0.4 grams in the product and strontium 0.1% to 0.02% of the total curie activity in the product. Iron removal steps have demonstrated the removal of as much iron as analyzed in the feed, but recontamination occurs by corrosion iof the stainless steel equipment used.

Future Development

Runs will be made to demonstrate the "One column - No Metathesis-Versene" ion exchange process for barium yield and lead, iron, sodium, and strontium decontamination. Equipment is being installed wholly of non-corrosive material to prevent iron recontamination of the product.

Three runs have been made so far centrifuging barium sulfate without lead carrier. With a barium concentration of 1 gram per 100 gallons, a steam jet feed rate of 2 liters per minute, and centrifugation at 3600 RPM in a 12" Bird centrifuge, extraction losses have varied from 13% to 25%. This shows so much promise of making a shorter and more simple procedure that a pump is being installed to feed at a slower feed rate. A "One column No Metathesis-Versene" process will be used for the final purification. One ion exchange run has already been made with barium losses of 3%, strontium reduced to 1% of the original curie activity, and sodium to 0.4 g in the product, with no concern for lead removal.

50-3-232

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FLS-275
Chemical Technology Division

To: F. L. Steahly

Date: March 15, 1950

From: I. R. Higgins

Report Period: 2/10/50 to 3/10/50

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Problem No. TDSI-34

MONTHLY REPORT

Title: Barium Separation and Purification - Unit Operations

Work by: I. R. Higgins, W. E. Shockley, D. B. Masters

Secret Notebook No. 80 and 90

A one-column Versene ion exchange step is planned for the final purification either with or without metathesis. A 3" x 7" Dowex 50 resin bed has been demonstrated to be adequate following metathesis with either citric acid or Versene as complexing agent. A 3" x 20" Dowex 50 resin bed is required if no metathesis step is employed, and current investigations are evaluating this latter process with Versene as complexing agent. Preliminary indications are that product from this process is well within the prescribed specifications on impurities. Total barium losses from prefiltration through the ion exchange purification steps do not exceed 1%.

Chemical procedures have been investigated for dissolving or loosening the siliceous crud from the slugs in order to eliminate the prefiltration step. All visible black crud was eliminated by alternate treatment with boiling 6 M HNO_3 (30 min.) and 6 M NaOH with H_2O_2 (1 hour) with a 1% U loss in 2 cycles, after the regular aluminum jacket removal (Hanford procedure). Filtration tests to date on the UNH solution after this type of crud removal were somewhat short of success as measured by completely removing the filter plugging agent or elimination of the need for a crud prefiltration.

Apparently the silicon content of the uranium slug itself is quite sufficient to plug the filter. Typical uranium slug metal contains 0.005 to 0.01% Si, or up to 0.35 grams per Hanford slug. Several runs demonstrated that solution from dissolving slug cores still plugs the filter. In this case, backwashing was sufficient to clear the filter.

Design is progressing on a filter for separation of lead-barium sulfate and carbonate precipitates, after prefiltration of the UNH with filter aid to remove filter plugging siliceous crud ~~derived from the jacket bonding agent~~.

Scouting runs indicated that the "cold" barium normally occurring in the bombarded slugs may be sufficient to carry the "hot" barium when centrifuged without lead carrier. A variable-flow pump will be used in place of a jet to feed the 12", 3600 RPM "Bird" centrifuge at a slower rate in order to improve the centrifugation of 1-1/2 - 6 grams of barium, as sulfate, from 100 gallons of 1.5 Sp. Gr. UNH solution. There are three objectives in this process: (1) elimination of the crud prefiltration - a brief chemical crud removal procedure would be adequate with the centrifuge operation since there is no concern for filter plugging; (2) lead separation steps could be eliminated without concern for lead being a final product contaminant; (3) without lead, a very much smaller ion exchange column (2" x 6") could possibly be used, and the product could be eluted directly into the shipping cone with no need of an intermediate noble-metal evaporator. The last-named advantage could also be realized if the "lead-removal-in-centrifuge-bowl-with-caustic" process developed earlier were used. The overall advantages are simplification in processing, and reduction in cost of the new installation since fewer pieces of equipment are required.

50-4-192 13

FIS-311
Chemical Technology Division

To: F. L. Steahly

From: I. R. Higgins

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Problem No. TDSI-

MONTHLY REPORT

Title: Barium Separation and Purification - Unit Operations

Work by: I. R. Higgins, W. E. Shockley, and D. B. Masters

Secret Notebook No. 80 and 90

When it was discovered that the barium product could be eluted in only a very slightly greater volume in the 3" x 20" column than the 3" x 7", it was decided to use metathesis and the 3" x 20" column and raise the moles of Versene from 0.52 to 0.96. This increases the process safety factor by reducing sulfate and increasing Versene, but keeping the amount of Versene per unit volume of resin below what was used in the "no-metathesis" runs (1.14 moles). This modified process is now being tested. An undesirable feature remaining in this process is the adjustment of pH of the feed solution to 6.5. The trend of development in the laboratory is to lower the Versene molarity, increase the pH to the point where pH is not critical, and increase the resin volume to avoid pH adjustment of the feed. This new procedure will be tested if and when the laboratory results indicate it is feasible.

During this period One-Column Versene Test Runs were made on the 3" x 20" Dowex 50 resin bed without metathesis, and on the 3" x 7" bed with metathesis. A total of 4 runs of each type were made with irregularly good results, because of inherent variations in process conditions which must be expected in normal operation.

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It was concluded that for both processes not enough safety factor was allowed in the moles of Versene used per run and in the amount of resin in the column to cover variances in sulfate concentration, pH, and total grams of barium and strontium present. In some runs, product has precipitated out in the column feed tank because of a higher than usual sulfate or lower pH. In other runs the barium losses were high in the feed waste or strontium waste indicating that the pH was too high or the resin volume too small. Both phenomena have not occurred in the same run indicating that although process conditions were set close to the "balance point", insufficient safety factor was allowed.

Centrifuging: A series of centrifuge runs were made in conjunction with ion exchange testing to test the centrifugation of barium sulfate without lead carrier and the centrifugation of lead-carried barium sulfate with lead removal in the centrifuge bowl. Barium losses without lead carrier, centrifuging at 2200 G, varied from 12% to 99%. There correlations with the grams of Ba present (1.5 to 6.0 grams per 100 gallons of UNH) or the rate of feed to the centrifuge (0.7 to 2.5 liters per minute) were insufficient to explain the barium losses. Since some unknown factor was envolved, the "no-lead" process was abandoned.

With lead carrier, the sulfate precipitate losses were less than 1%. The bulk of the lead can be removed by treating the sulfate cake with caustic-carbonate solution and centrifuging the barium (sulfate or carbonate) precipitate from the plumbite solution with barium losses of about 3%-5%. It was discovered that a high percentage of the metathesized barium sulfate would not dissolve in acid probably because the large heel in the centrifuge bowl prevented complete removal of sulfates in the centrifuge bowl washes. For this reason and because final design of the alternative filter installation is complete, centrifuge runs have been discontinued.

50-5-214 15

FLS-340

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To: F. L. Steahly

From: I. R. Higgins

Date: May 15, 1950

Report Period: 2/10/50-5/10/50

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TDS1-34

Dec

QUARTERLY REPORT

Title: RaLa Process - Unit Operations, Part I Ion Exchange Development

Work by: I. R. Higgins, W. E. Shockley, D. B. Masters

Secret Notebook no. CL-90, CL-288,

SUMMARY

Dvelopment during this period has been concentrated on a "one column Versene" process, leading to a definitive decision to recommend including the metathesis step, and using 1.0 moles of Versene, feed pH 6.5 and a 3" x 24" Dowex 50 resin bed. These conditions were picked to allow plenty of safety factor for high barium yield and effective barium and strontium separation for handling a lead-barium sulfate cake which has been only about 99% metathesized. A total of 12 "one column Versene" runs have been completed. Sulfate precipitate is found in the process tanks when the sulfate content is too high or when the pH or Versene concentration is too low. High barium losses and poor strontium removal occur when the pH or Versene concentration is too high or the resin volume too small. Table I indicates, the very high degree of metathesis required to render all barium soluble in dilute nitric acid and, the importance of using a barium sulfate dissolving reagent, as Versene, in the process. Table II summarizes the significance data in the Versene process. Apparently pH 6.5 is the upper limit for the low barium loss. Runs are now in progress to determine the lower limit of pH.

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Resin Bed Pressure Drop: In order to determine if pressure was required on the ion exchange feed tank to overcome the resin bed resistance, pressure drop was measured on a 3" x 7" and 3" x 18" resin bed with and without vapor locking. Table III indicates that the bed resistance to flow at the rates planned, 0.5 ml/min/cm^2, is very small even with vapor locking.

TABLE I

Completeness of Metathesis

Based on amount of barium precipitated from the low acid solution of the metathesized cake

Run	Grams Ba	% Ba Precipitated	% Metathesis of Total Sulfate Cake	
				Sulfate Analysis
4	1	83	98.6	
5	1	4	99.9	—
8	1	9	99.8	—
17	1	95	98.4	—
24	1	20	99.7	—
26	1	63	98.9	98.7
27	1	19	99.7	97.9
28	1	6	99.9	99.5
30	1	6	99.9	97.6
33	1	9	99.8	—
45	2	2	99.9	100
46	2	3	99.9	—
47	0.5	3	99.9	—
49	2.0	90	97.0	—
Average		30	99.5	

Note - % completion of metathesis calculated assuming $BaSO_4$ solubility in weakly acid metathesis solution equal to published solubility of $BaSO_4$ in water.

TABLE II

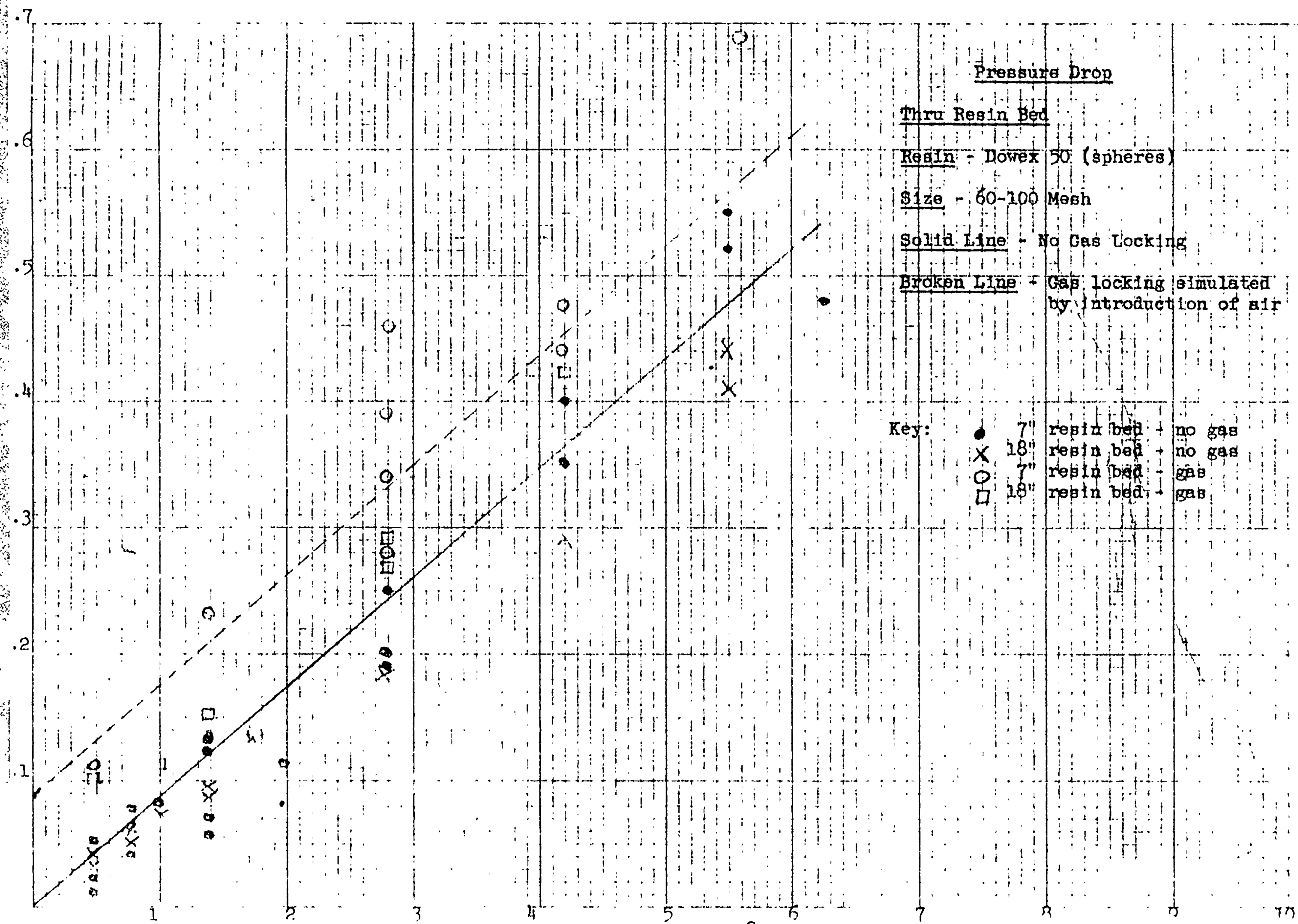
Critical Factors in the "One Column Versene" Process for Low Barium Losses and

High Barium-Strontium Separation Process Steps

1. Solution of the lead-barium sülfate or carbonate precipitate in nitric acid or Versene.
2. Adjustment of pH and feeding to the Dowex 50 resin column.
3. Elution of any remaining strontium with Versene and pH 6.3.
4. Elution of the sodium with HCl.
5. Elution of the barium with 6 M HNO_3

Run	Metathesis	Column Size	Feed			Percent Barium Losses				Percent Strontium in Product
			Mols Versene	pH	Grams Ba and Sr	Settled in Tanks	Column Breakthru	Strontium Waste	Sodium Waste	
706-D	Yes	3x7"	0.65	6.0	1	52.2	0.6	0.5	0.1	0.66
36*	No	3x20"	1.14	6.3	1	13.4	0.3	0.3	0.1	1.92
37*	No	3x20"	1.14	6.4	1	54.2	0.3	0.1	0.1	0.30
38*	No	3x20"	1.14	6.5	1	12.1	2.2	3.3	0.9	0.59
42	No	3x20"	1.14	6.5	1	0.9	76.0	5.2	1.5	0.37
43	Yes	3x6"	0.52	6.1	2	1.2	0.9	84.0	0.7	2.10
44	Yes	3x19"	0.96	6.5	4	5.2	0.5	0.7	4.3	0.95
45	Yes	3x19"	0;96	6.5	4	1.2	0.2	3.5	1.0	0.17
46	Yes	3x23"	1.40	6.5	4	0.5	1.3	4.0	1.5	0.03
47	Yes	3x23"	1.0	6.5	1	1.2	0.2	0.2	0.03	0.03
48	Yes	3x23"	1.0	6.8	4	2.0	14.5	6.8	2.1	0.001
49	Yes	3x23"	1.0	6.7	4	1.8	26.9	11.5	3.4	0.07

TABLE III



Pressure Drop
Thru Resin Bed
Resin - Dowex 50 (spheres)
Size - 60-100 Mesh
Solid Line - No Gas Locking
Broken Line - Gas locking simulated by introduction of air
Key:
● 7" resin bed - no gas
X 18" resin bed - no gas
O 7" resin bed - gas
□ 18" resin bed - gas
.7
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50-8-153

FLS-414

SECRET ROUGH DRAFT

To: F. L. Steahly

From: I. R. Higgins

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Date: August 2, 1950

Report Period:
6-10-50 to 7-14-50

Approved - J. C. Davis

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No. 1 of ... copies, Series ...

TDS1-34

QUARTERLY REPORT

Title: RaLa Process - Unit Operations, Part I - Ion Exchange Development

Work by: I. R. Higgins, W. E. Shockley, D. B. Masters, and D. L. Foster

Secret Notebook No. CL-288

The RaLa ion exchange development has been completed. A total of 8 demonstration runs have been completed using the One-Column-Versene Process. The "Hemphill One-Drop pH Meter" was used in the last two runs to adjust the "hot" Versene feed to pH 6.4. The Sr in the last run was higher than usual possibly because the resin bed was 2" deeper than usual in the column, and additional eluting agent was not provided. Also, the ionization chamber monitoring the effluent was out of service and the Sr elution curve could not be observed in the last 2 runs, 5 liters of 2 M HCl was used instead of 10 l of 1M in order to reduce the Na elution time and the 5 liter volume proved to be insufficient. Since the last run was made the Na specifications have been reduced from 10 mg. to 1 mg. in the product.

The Dow Chemical Company is being contacted to determine if Fe-free resin can be obtained. Runs 44 through 51 were made on the same batch of resin and it is noted that the iron in the product decreased. Run 56 was made on the same batch used the 4th time and run 58 was made on a new batch the 1st time. Even if Fe free resin can be obtained, provision will be made in operations to pre-elute the resin with HNO_3 before use.

SECRET ROUGH DRAFT

Table I

Barium Losses and Purity for the
One Column Versene Process

Resin - Dowex 50 60-100 Mesh
Column - 3" x 23" (Run 58 25")

Feed - 15 l 1 Mole Versene and 0.1 to 0.3 mols of Fe-3 Specific Versene pH 6.3 - 6.5

Sr Elution - 3.5 l 0.07 mols Versene pH 6.3

Na Elution - 10 l 1 M HCl
or 5 l 2 M HCl (Runs 56 and 58)

Product Elution - 5 l 6 M HNO_3

Column Clean-up - 5 l 0.1 M Tetra sodium Versene

Run	Ba Losses			Contaminants in Product			
	Undissolved Sulfate	Ion Exchange Process	Overall	Sr % of Ba	Fe mg	Pb mg	Na Grams
44	5.2	5.2	11.0	0.95	178	<40	0.6
45	1.2	5.8	7.0	0.17	162	<18	0.1
46	0.5	6.9	7.4	0.03	196	<25	0.7
47	1.2	~~0.5~~ 0.4	1.6	0.03	86	<30	0.6
50	0.6	0.1	0.7	0.44	13	<30	0.4
51	0.6	0.2	0.8	0.16	14	<33	0.3
56	1.2	0.4	1.6	0.25	27	<24	3.3
58	1.3	0.1	1.4	6.2	74	<26	8.8

50-6-226 21

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FLS-375
Chemical Technology Division

To: F. L. Steahly

Date: June 14, 1950

From: I. R. Higgins

Report Period: 5/10-6/10/50

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TD51-28

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MONTHLY REPORT

Title: RaLa Process - Unit Operations, Part I - Ion Exchange Development

Work by: I. R. Higgins, H. O. Weeren, W. E. Shockley, and D. B. Masters

Secret Notebook No. CL-90, CL-288

SUMMARY

Two additional demonstrating runs were completed for a total of six proving runs on the recommended one-column-Versene barium ion exchange process with eminently satisfactory results. Ba losses were less than 1%, Sr activity less than 0.5% of the Ba activity, Na less than 0.5 g, Fe about 15 mg., and Pb less than 35 mg. in the product. The process conditions have been set at, a 3" x 24" Dowex 50 column, 1.0 mole of Versene and 0.3 mole of Fe-3 specific in the feed adjusted to pH 6.3 - 6.5. Additional runs will be made only if deemed necessaryto further prove the reliability of the process. See Table I.

Table I

Barium Losses and Purity for the One Column Versene Process

Resin - Dowex 50, 60-100 Mesh

Column - 3" x 23"

Feed 1 Mole Versene and 0.1 to 0.3 Mols

Fe^3 Specific pH 6.3 - 6.5

Sr Elution - 0.07 Mols Versene pH 6.3

Na Elution - 1 M HCl

Product Elution - 6 M HNO_3

Column Cleanup - Tetra-Sodium-Versene pH 11

Run	Barium Losses			Contaminants in Product			
	Undissolved Sulfate	Ion Exchange Process	Overall Process	Sr % of Ba	Fe mg.	Pb mg.	Na Grams
44	5.2	5.2	11.0	0.95	178	< 40	0.6
45	1.2	5.8	7.0	0.17	162	< 18	0.1
46	0.5	6.9	7.4	0.03	196	< 25	0.7
47	1.2	0.4	1.6	0.03	86	< 30	0.6
50	0.6	0.1	0.7	0.44	13	< 30	0.4
51	0.6	0.2	0.8	0.16	14	< 33	0.3

[redacted]

50-6-229 23

FLS-378
Chemical Technology Division

To: F. L. Steahly

Date: June 15, 1950

From: I. R. Higgins

Report Period: 5-10 to 6-10-50

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TDS1-34

MONTHLY REPORT

Title: Sr^{90} Extraction and Partial Purification in the Unit Operations RaLa Development Equipment

Work by: I. R. Higgins, H. O. Weeren, W. E. Shockley and D. B. Masters

Secret Notebook No. CL-288

SUMMERY

An unusually large request for Sr^{90} was received by the Isotope Production Department, and the Unit Operations Section installation for Ba^{140} was the most suitable facility immediately available for extraction and concentration of their source material. Only minor process changes were necessary for Sr production. The runs were made not only to assist the Production Department, but also to establish confidence in the versatility of the Dowex-50-Versene system for producing Ba, Sr, or other isotopes. Because of the higher solubility product of $SrSO_4$ over $BaSO_4$, the $PbSO_4$ carrying was not nearly as complete. Five times the amount of Pb was used that would carry all the Ba and about 90% of the Sr was carried. The higher solubility product of $SrSO_4$ was an advantage in preparing the feed for the ion exchange-Versene process because higher sulfate concentration could be tolerated without precipitating $SrSO_4$ in the presence of Versene complexing agent. The sulfate cake was not metathesized and the Versene pH adjusted to 5.5-5.8 in the feed.

[redacted]

In the first two runs, the $PbSO_4$ extraction losses were 6.5% and 5.8% respectively. This loss is considered to be Sr not carried with the lead because a dozen runs are available to show that Ba losses using $PbSO_4$ carrier are less than 1%. The ion exchange losses on the first 2 runs were 0.03% and 0.8%. 6.6 curies of Sr^{90} were produced from the 1st run and analysis of the others is not available yet.

In the 3rd run that proverbial hot region over-ran its boundaries. The mechanical agitator failed resulting in poor mixing of the sulfuric acid added, with formation of solid UO_2SO_4. The $PbSO_4$ could not be suspended to jet to the centrifuge. Since the Pb was not all in the centrifuge bowl (unknown at the time) adding the usual amount of Versene caused a large break through loss on the ion exchange column. About 35% of the product was finally recovered.

HSA/DOSE RECONSTRUCTION

The following documents are part of document number **CF-52-3-62.** The list contains the document CF number, the page number in CF-52-3-62 where the document starts, and the title of the document.

49-7-280	17	Barium 140 Separation Development in the Semi-Works - June 10 to July 10, 1949
49-8-312	21	Barium 140 Separations Development in Semi-Works - May to August 1949
49-9-257	29	Barium 140 Development in the Semi-Works - August 9 to Sept. 9, 1949
49-10-260	37	Barium 140 development in the Semi-Works - Sept. 10 to Oct 10, 1949
50-5-215	2	RaLa Process - Unit Operations, Part II Auxiliary Equipment Development - Feb. 10 to May 10, 1950
50-6-221	11	RaLa Process - Unit Operations, Part II Auxiliary Equipment Development - May 10 to June 10, 1950

3/15/95

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RALA - SEMI WORKS DEVELOPMENT (1949 -)

PRECIPITATION AND AUXILIARY STUDY

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FLS-341 RaLa Process - Unit Operations, Part II Auxiliary Equipment Development, Period 2/10/50 - 5/10/50.

FLS-370 RaLa Process - Unit Operations, Part II Auxiliary Equipment Development, Period 5/10/50 - 6/10/50.

Barium 140 Separation Development in the Semi-Works.

FLS-97 Barium 140 Separation Development in the Semi-Works, Period 6/10/49 - 7/10/49.

FLS-113 Barium 140 Separations Development in Semi-Works, Period May - August, 1949.

FLS-136 Barium 140 Development in the Semi-Works, Period 8/9/49 - 9/9/49.

FLS-161 Barium 140 Development in the Semi-Works, Period 9/10/49 - 10/10/49.

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[redacted]

[redacted]

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[redacted]

50-5-215

2

FLS-341
Chemical Technology Division

To: F. L. Steahly

From: I. R. Higgins

Date: May 15, 1950

Report Period: 2/10/50 - 5/10/50

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TDS1-34

QUARTERLY REPORT

Title: RaLa Process - Unit Operations, Part II Auxiliary Equipment Development

Work by: I. R. Higgins, W. E. Shockley, D. B. Masters, H. O. Weeren, G. A. West, and C. D. Watson

Secret Notebook No. CL-80, CL-132, CL-82

1.0 Summary and Introduction

Various pieces of auxiliary equipment for the new RaLa change-over are being tested for operating characteristics and reliability before final installation.

(1) Full scale crud and process filters with exact space arrangement to determine filtration rates, filter aid handling, and operating techniques.

(2) Simulated product evaporation to determine quantitative transfer conditions to the shipping cone.

(3) Surface evaporation from the shipping cone to determine the optimum operating conditions for rapid evaporation without splashing and,

(4) Testing steam jets for use as a vacuum source. Preliminary indications are that all items can be used, some with modifications.

[redacted]

3

2.0 Experimental

2.1 Crud and Process Filtration

The Crud Filter: has been tested twice at full scale and the process filter once. 180 liters of 1.5 Sp. Gr. UNH was filtered through the 1.33 sq. ft. precoated star filter in 45 minutes using 5 g/l of 545 filter aid slurried in the crud containing UNH with a "Ruch" air agitator. The agitator formed a heavy mist when the liquid level was below one foot and an estimated 50 grams of the 9000 grams of filter aid was left in the center of the tank. The filter aid was completely backwashed with 60-80 l water.

One Process Filter Run: has been made at full scale with the 0.55 sq. ft. Carpenter 20 "G" porosity filter using 90 g Pb, 2 g Ba, and 2 g Sr slurried in 180 liters of uranium solution at 3.5 M sulfuric acid, sp. gr. 1.5. The vacuum and transfer was made with a 3/4" S-K steam jet in 2 hours using 100# steam and maintaining 23"-25" vacuum. The filter was backwashed once during the run to unclog the filter. The total dilution from the steam jet was 57%. The precipitate was completely washed back to the precipitator with 10 l of water.

2.2 The Product Evaporator: was installed and no runs have yet been made to demonstrate quantitative product removal.

2.3 Shipping Cone: several tests have been made with total evaporation time from 4 to 9 hours. Ideal conditions of temperature and air flow have not been determined because in most runs agitation and splashing have occurred by the air flow leaking around the charging header and cone. The tightness of the cone fit determining whether splashing occurs or not. Evaporation without splashing was achieved at 0.05 # air/min. and 150°C in 7 hours with liquid temperature of 50°C under 20" Hg pressure.

2.4 Steam Jet Exhauster

The optimum operating conditions for the 3/4" S and K exhauster was found to be between 80 psig, spindle 1/2 way open - and 100 psig, spindle 1/4 open; with production of 27" Hg vacuum. For use as a vacuum source, a water-jacketed condenser is required to condense 1# of steam per minute mixed with 0.1# of air per minute. A water jet used as a contact condenser would discharge about 4 GPM to the "hot" drain, and would overload the drain system.

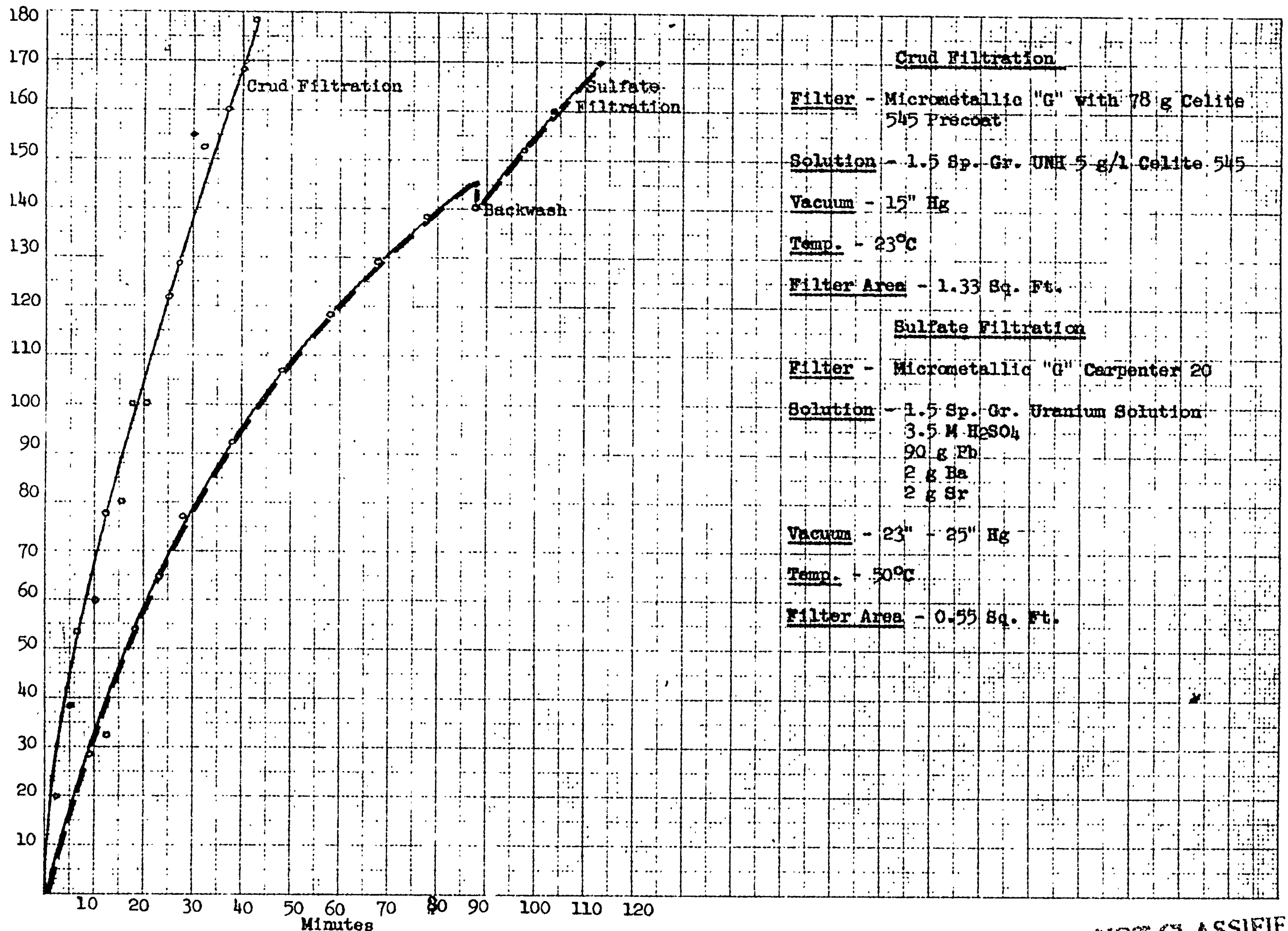

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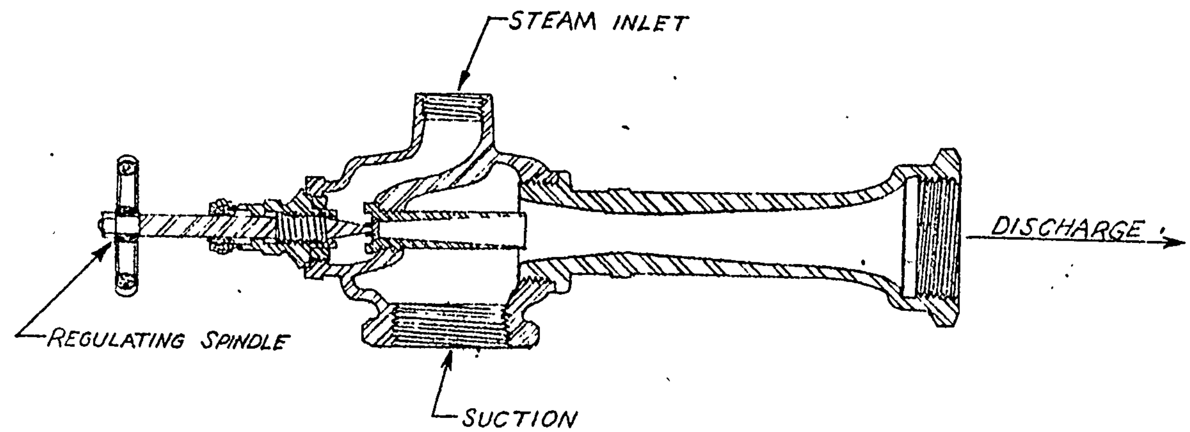
FIG. 1



NOTE: Jet Dwg. reproduced from S & K Bulletin No. 4-E.

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STEAM JET EXHAUSTER – (S & K FIG. 431-A)			
DRAWN BY GAN.	DATE 4-7-50	SCALE NONE	
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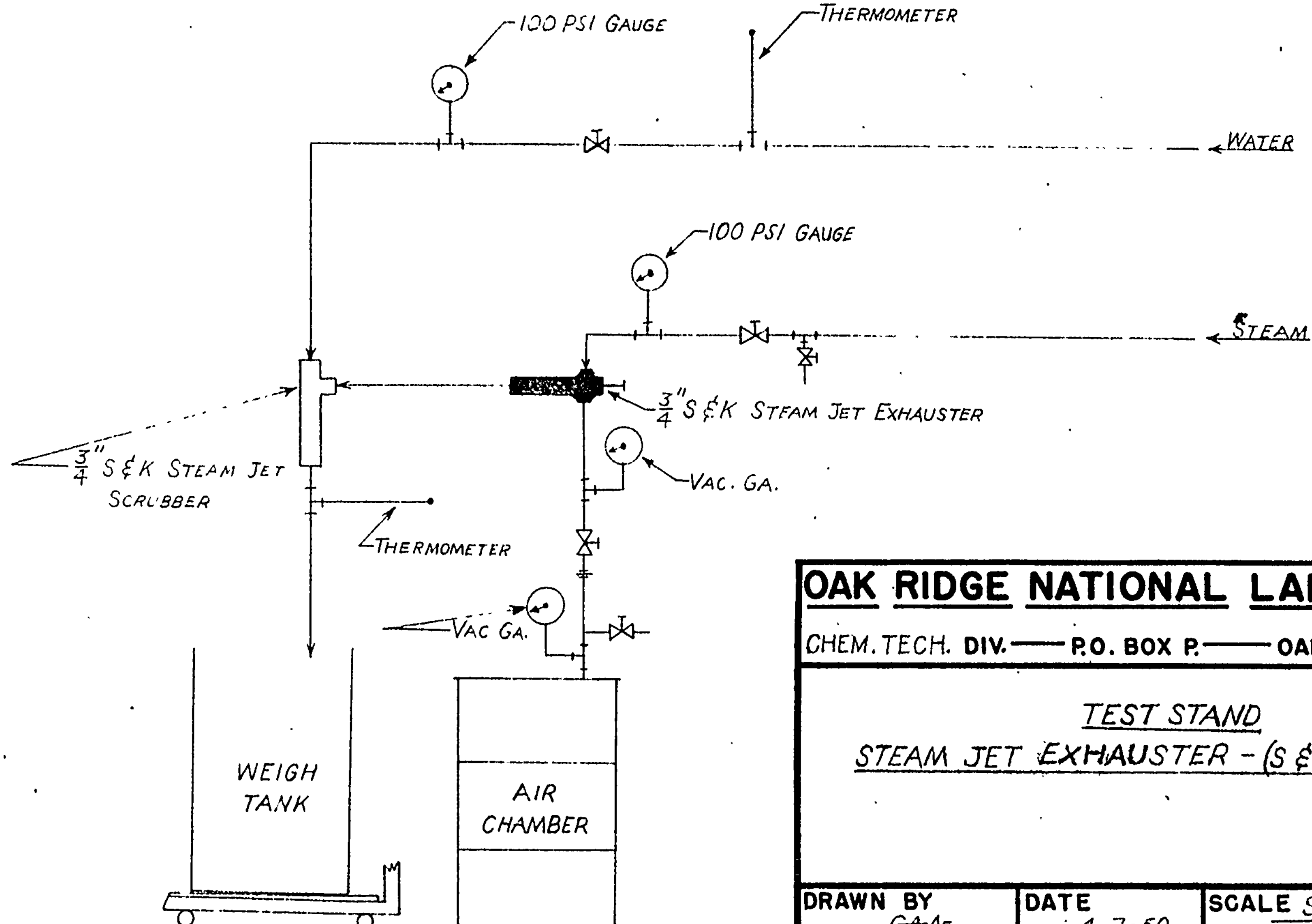
FIG. 2



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TEST STAND

STEAM JET EXHAUSTER - (S & K FIG. 431-A)

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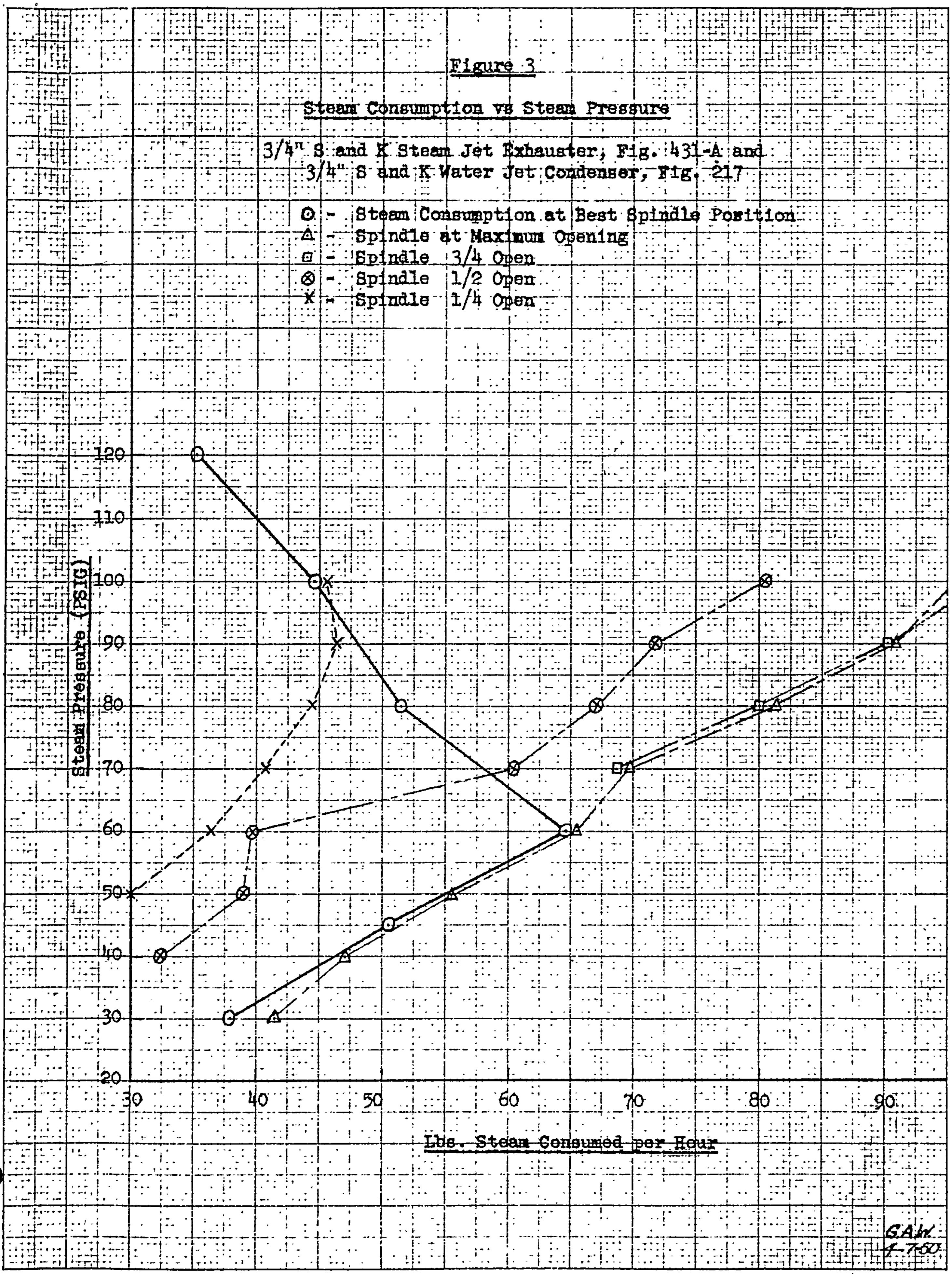

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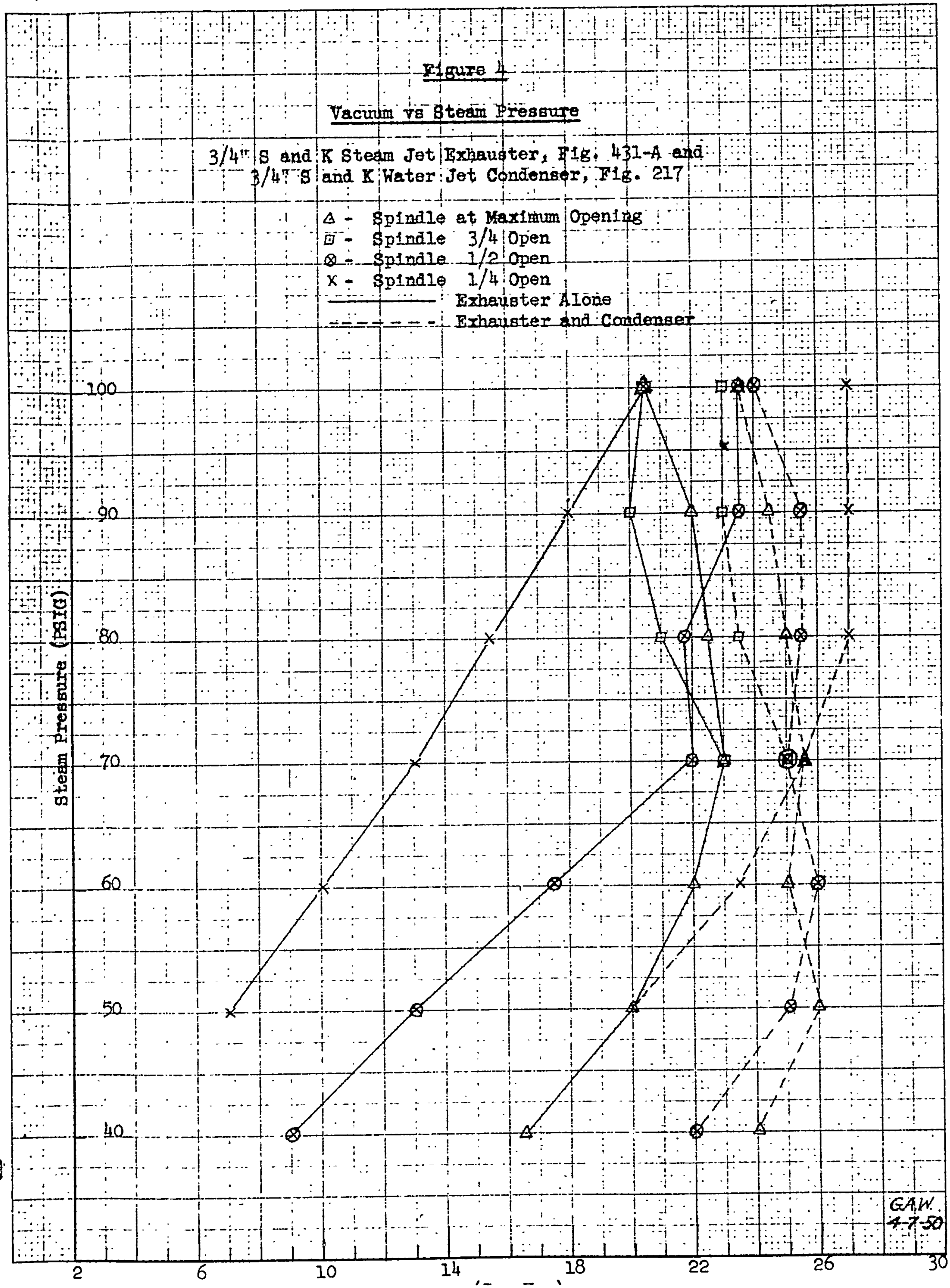

Figure 4
Vacuum vs Steam Pressure
3/4" S and K Steam Jet Exhauster, Fig. 431-A and
3/4" S and K Water Jet Condenser, Fig. 217
△ - Spindle at Maximum Opening
☐ - Spindle 3/4 Open
⊗ - Spindle 1/2 Open
X - Spindle 1/4 Open
——— Exhauster Alone
- - - - Exhauster and Condenser
Steam Pressure (PSIG)
100
90
80
70
60
50
40
2
6
10
14
18
22
26
30
GAW
4-7-50

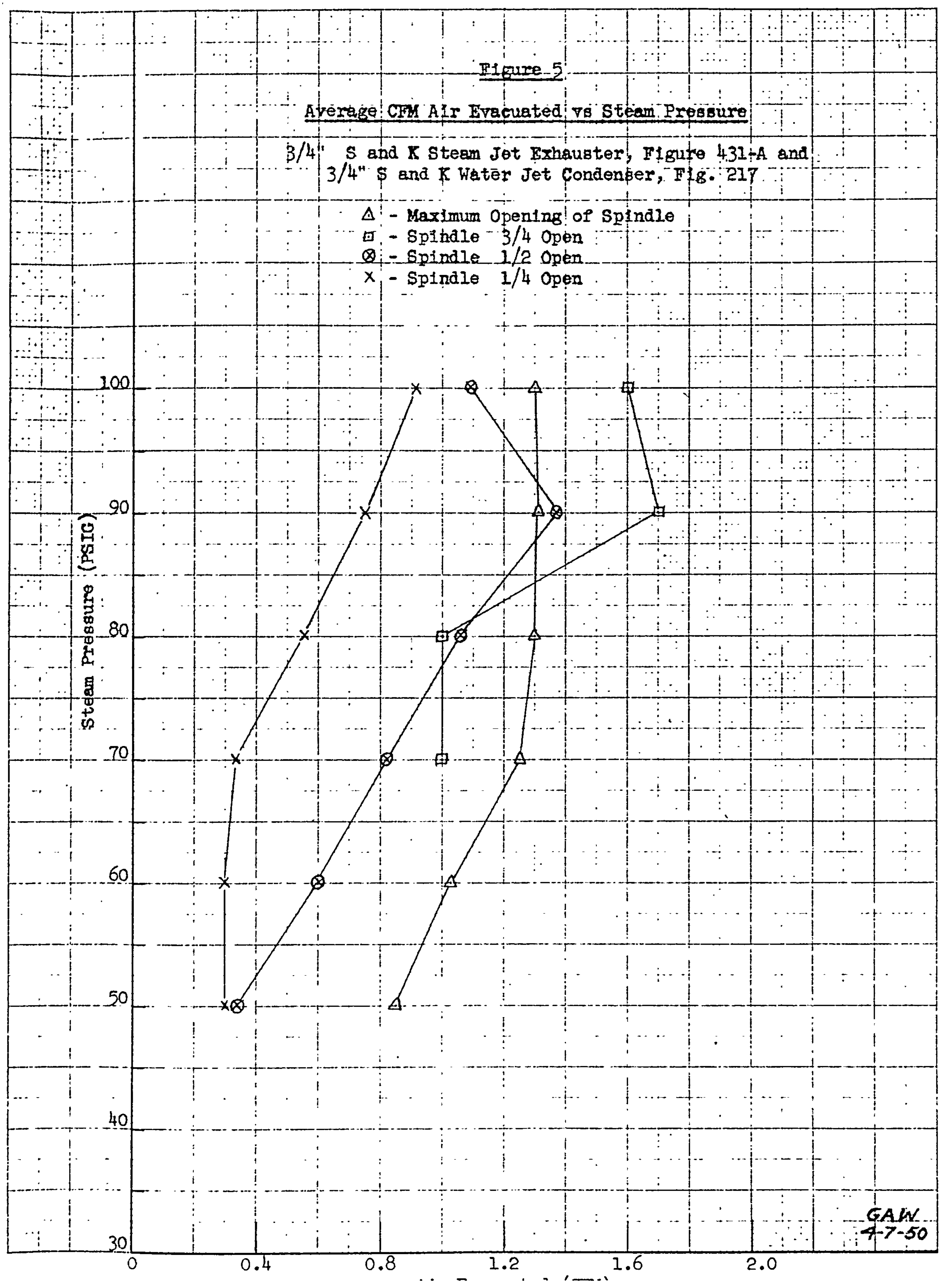

Figure 5

Average CFM Air Evacuated vs Steam Pressure

3/4" S and K Steam Jet Exhauster, Figure 431-A and
3/4" S and K Water Jet Condenser, Fig. 217

50-6-221 11

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FLS-370
Chemical Technology Division

To: F. L. Steahly

Date: June 14, 1950

From: I. R. Higgins

Report Period: 5-10 to 6-10-50

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TD51-34

MONTHLY REPORT

Title: RaLa Process - Unit Operations, Part II Auxiliary Equipment Development

Work by: I. R. Higgins, W. E. Shockley, D. B. Masters and H. O. Weeren

Secret Notebook No.: CL-80, CL-132

SUMMARY

A full scale crud and process filter, a product evaporator, a tube bundle heat exchanger, a liquid level transmission system, and a shipping cone evaporator have been tested for the new RaLa equipment change-over with satisfaction except for some minor changes.

(1) Full Scale "Crud" and Process Filter Test

A full RaLa batch of Hanford slugs was dissolved and processed at full scale under actual space arrangement of the filters. One hundred forty liters of "crud" containing UNH at Sp. Gr. 1.62 at 25°C was filtered in 40 minutes through the 1.33 sq. ft. precoated star "G" porosity filter using 5 g/l of Celite 545 filter aid. One hundred eighty five liters of $PbSO_4$ slurry in UO_2SO_4 solution was filtered through the 0.55 sq. ft. Carpenter 20 "C" porosity filter at Sp. Gr. 1.59 and 50°C in 115 minutes. The flow rate started at 3 liters/minute and ended at 1 liter/minute. The steam jet dilution varied from 22% to 45% over this flow rate.

[redacted]

(2) Product Evaporator - Operation And Quantitative Transfer

Ba^{140} tracer runs with full gram quantities of "dead" Ba and HNO_3 were made to determine evaporation characteristics and transfer efficiencies. Two runs were made by boiling the 5 l of 6 M HNO_3 ion exchange product solution to 1 liter and precipitating the $Ba(NO_3)_2$ out with fuming nitric acid; with removal of the nitric acid through a filter stick. One run was made by boiling the 6 M HNO_3 to dryness. Inn all runs, the $Ba(NO_3)_2$ was returned to solution by reflux boiling 300 ml of water. The 300 ml of $Ba(NO_3)_2$ solution was drawn off and followed with 2-100 ml portions of water. The losses were 1.7%, 1.3%, and 0.5% which represents heel left in the vessel and not solid undissolved barium. The losses in the fuming nitric acid waste were 1.6%, and 0.8%. The condensate waste from the evaporation were of the order of 0.01%.

(3) Tube Bundle Heat Exchanger Heat Transfer Test

In the new RaLa equipment change over, steam jets are being used in several places for pulling a vacuum or transferring hot solutions. One or two of these jets will be pulling through a filter and there will not always be a steady stream of liquid, but a mixture of hot liquid and steam. To condense the steam and scrub spray from the jet exhaust, "Ross" compact tube bundle heat exchangers will be used. The heat transfer coefficient across this exchanger was found to be 73. Wtih 8% air (by weight) the coefficient was 77, with 15% air 82, 24% air 112, 30% air 104, and 39% air 109. The condenser was considered satisfactory and will be used.

(4) Moore Products "Nullmatic" Transmission System

A Moore Products "Nullmatic" transmission system for liquid level is being tested for tanks under vacuum and pressure containing highly active solutions. The instrument checked with two separate tank calibrations and returned to the same zero point at least a half dozen different times. When liquid boils in a tank the level indicator jumps like a manometer does because of the percolation of the boiling liquid up through the dip tube. The true liquid level can only be obtained after cutting off the heat supply. The instrument was considered reliable and will be used.

(5) Surface Evaporation in the Shipping Cone

A new and less massive charging head has been designed and is being installed for testing which is expected to operate with less heat loss and a more uniform distribution of hot air. An actual shipping cone has been received which is machined to fit the charging head closely thus eliminating the cold air leak around the seal. Final test will be made with this new equipment.

[redacted]

[redacted]

Technical Division
Chemical Process
Development Section

To: F. L. Steahly

From: I. R. Higgins

Date: June 10, 1949

Report Period: 5/6/49 to 6/6/49

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Problem No. TDSI-34

Part II

MONTHLY REPORT

Title: Barium 140 Separation Development in the Semi-Works

Work by: I. R. Higgins, R. H. Vaughn, W. A. Horne, J. B. Goodman, D. B. Masters

Secret Notebook No.

SUMMARY

Two cold Pb-Ba precipitation runs have been made to test the filter stick, train the operators, and determine the filtration efficiency. The 700 x 60 stainless steel screen alone allowed the Pb SO_4 and Pb CO_3 precipitater to pass through. The 10 micron micrometallic "G" filter stopped the Pb SO_4 but not the Pb CO_3. The Pb CO_3 was not digested according to the flowsheet procedure. A flowsheet precipitation will be tried with Ba 140 tracer.

Testing the centrifuge has been delayed because of motor troubles. A run is in progress using the low speed of the centrifuge, 900 RPM. Water can be steam jetted to the centrifuge at a controlled rate of 0.7 liters per minute. The heavier 50% UNH solution containing the Pb SO_4 precipitated cannot be jetted slower than 2 liters per minute. At the low RPM of 900 the effluent was clear at 2-4 liters per minute feed.

C [redacted]

Hot flowsheet runs will be made during June with the filter and the centrifuge for separating Pb SO_4 and Pb CO_3 precipitates.

Other experiments planned are:

(1) metathesis (Pb SO $\rightarrow$ Pb CO_3) in the centrifuge bowl without dilution.

(2) separation of Pb and Ba in the centrifuge bowl by solubilizing the Pb with caustic.

(3) centrifugation of Ba SO_4 precipitate without Pb carrier.

Ion Exchange equipment for testing Blanco flowsheets for final purification of Ba will be set up in Cell #3.

Results and Discussion

Some study has been made of the solubility of Pb and Ba sulfate and carbonate precipitates in carbonate and caustic solutions. If Ba CO_3 is sufficiently insoluble in K_2CO_3 it may be possible to metathesize in the centrifuge bowl. If Ba CO_3 is insoluble in KOH it may be possible to separate Pb and Ba in the centrifuge bowl by forming Pb O_2^-. If Ba SO_4 is soluble in carbonate free caustic both the metathessis and electrolysis steps may be skipped by feeding Pb O_2^- and Ba (OH) to an ion exchange separation column (R. E. Blanco).

Table I shows the solubility of Ba CO_3 in K_2CO_3 and KOH. Table II indicates the solubility of Ba SO_4 in KOH solution (not carbonate free).

TABLE I

Solubility of Ba CO_3 in 4 M K_2 CO_3 and 4 M K_2CO_3 plus 1 M KOH

	g/l Ba
Feed Ba^{++}	5.3
4 M K_2CO_3 Effluent	0.05
4 M K_2CO_3 plus 1 M KOH Effuent	0.019

[redacted]

Table I indicates that Ba is not soluble in 4 M $K_2 CO_3$ therefore metathesis is possible in the centrifuge bowl. Also Ba CO_3 is not soluble with added KOH. Therefore Pb and Ba separation is possible if sufficient centrifugal force is available to quantitative separate a small quantity of finely divided Ba CO_3.

TABLE II

Solubility of Ba SO_4 in 4 M $K_2 CO_3$ and in 4 M KOH

	g/l Ba
Feed - Ba SO_4	5.3
4 M $K_2 CO_3$ Effluent	$<$ 0.005
4 M KOH Effluent (not Carbonate free)	0.7

Table II indicates that Ba SO_4 is not solubalized by $K_2 CO_3$ but probably is in carbonate free KOH. If Ba SO_4 can be quantatively converted to Ba $(OH)_2$ by this method it is possible to eliminate the present metathesis and electrolytes steps by R. E. Blanco's ion exchange procedure.

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49-7-280

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FLS-97
Technical Division
Chemical Process
Development Section

To: F. L. Steahly

From: I. R. Higgins

Date: July 10, 1949

Report Period: 6-10-49 to 7-10-

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Problem No. TDSI-34

Part III

M O N T H L Y   R E P O R T

Title: Barium 140 Separation Development in the Semi-Works

Work by: Higgins, Vaughn, Horne, Goodman, Masters

Secret Notebook No.

SUMMARY

Two "hot" filtration runs have demonstrated total losses of about 0.3% for the separation of barium from dissolver metal solution. Preliminary experiments show promise for the separation of lead and barium centrifugally. Resin adsorption equipment will be installed and ready for cold runs 17 July, 1949.

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Run No.		Remarks
3		A cold run for equipment tests. No analytical data reported.
3A and 6	Cold Tracer	Separation of Pb and Barium by solubilizing the lead with caustic and removing the barium precipitate centrifugally.
4 and 5		Filtration separation of the barium and lead according to present Rala procedures.

Centrifugal Separation of Pb and Ba

The present RaLa process employs precipitation of lead sulfate to facilitate removal of barium from the dissolver solution. The sulphate is then metathezed to the carbonate which is dissolved in nitric acid and electrolyzed to separate the lead from the barium product solution. It was proposed that the metathesized carbonate precipitate, containing lead and barium, be treated with a solution 3 M in KOH and 0.5 M in K_2CO_3 to solubilize the Pb, and be centrifuged to separate the barium carbonate. A cold run (3A) showed promise. 99.6% of the lead being removed in two treatments, calculated on the reduction of the lead to barium ratio of the feed and product samples.

A hot run (Run #6) was made to confirm these results, but a motor failure limited the centrifuge to a low speed (900 RPM, about 100 g's versus 1600 g obtainable at full speed, 3600 RPM) and the data are inconclusive. Nevertheless, a lead-Barium ratio reduction of 90% under these circumstances is encourageing and further investigation of this method of separation is clearly justified.

Filtration

Present RaLa process employs decantation which is time-consuming and mechanically inefficient. Two hot runs were made using a miro-metallic "G" filter. Filtration heels equal to the RALA plants decantation heels were deliberately left

[redacted]

in run 4 to duplicate exactly plant washing and metathesis conditions. Metathesis was incomplete as indicated by the difference between the yield and material balance.

Run 5 was made with as little heel as practicable in the filter tank, and the quantity of metathesis solution was generous to avoid incomplete metathesis.

Filtration Data

Run	Losses (in hundredths of one percent)											% Total Loss	% Yield	% Mat'l Bal.
	SO_4 Precipitation						Metathesis							
	Metal Solution	Washes					Metathesis		Wash					
		1	2	3	4	5	1	2	1	2	3			
4	2.6	0.7	0.5	0.2	0.1	0.6	1.2	0.7	0.6	4	10.5	0.22	16.7	113
5	8.5	0.5	0.2	0.5	0.1	0.5	3.6	4.0	2.0	2.2	–	0.22	96.5	96.[illegible]

Filter media were tested to determine the optimum porosity. Micro-metallic media F G and H were compared, with a metathezized lead carbonate slurry. Comparative times required for filtration of two liters of slurry were:

	Time required	Filtrate
H	7 minutes	Water clear
G	2 minutes	perceptibly turbid
F	7 minutes	Cloudy

Based upon this, and the excellent results of runs 4 and 5, the G grade media will be continued in service.

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Equipment Failures - Centrifuge

The Bird 3-speed centrifuge motor high-speed coil burned out three times. The failure was attributed to failure of Solenoid contactors in the switch gear. Probably, temporary under voltage (during startup of other motors on the same line) permitted the solenoid contactors to relax, resulting in high internal over loads in motor field windings. The motor is being rewound to preclude internal overloads, but at the sacrifice of the intermediate speed. Also, an individual line supply is being installed along with new switch gear to minimize the possibility of another motor failure.

Resin Column

A full scale resin adsorption column is being erected in cell 3 which will be used for tracer-level hot-run testing of the resin process proposed by Ray Blanco for purification of the Barium 140. The Barium product of the metathesis will be siphoned from cell 4 to a feed tank in cell 3. The barium will be separated from its contaminant with selective elutriants and the product solution, about 5 liters in volume, evaporated in the product receiver to approximately 500 ml.

Equipment should be installed and ready for cold runs in one week.

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21

FLS-113
Technical Division
Chemical Process
Development Section

To: F. L. Steahly

From: I. R. Higgins

Date: 10 August, 1949

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Report Period:
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Problem No. TDSI-34

QUARTERLY REPORT

Title: Barium 140 Separations Development in Semi-Works

Work by: I. R. Higgins, R. H. Vaughn, W. A. Horne, R. N. Saleeby, J. B. Goodman, D. B. Masters, W. R. Winsbro, and W. E. Unger

INTRODUCTION AND SUMMARY

Barium 140 from Hanford-irradiated slugs is now produced in equipment designed and erected under the stress of wartime emergency conditions. The present process involves precipitating the barium as a sulphate from a nitric acid slug solution using lead as a carrier. The sulphate precipitates are separated from the slug solution by decantation, metathesized to carbonates, dissolved in nitric acid and electrolyzed to plate out the lead carrier. The product is purified by precipitation from nitric acid and HCl-Ether over a sintered glass filter.

Waste losses have varied widely but have always been high, attributable principally to the mechanical inefficiency of the decantation operation. Centrifugation and filtration were proposed as alternatives and half-scale equipment was accordingly installed in cell #4, Semi-Works for testing and to determine what process variations, if any, were advisable. Investigatory work has been in accord with the following outline:

[redacted]

1. Sulphate separation step

   A. By filtration

   B. By centrifugation

      a. with lead carrier to aid precipitation

      b. without lead carrier.

2. Methathesis (conversion of sulphate precipitate to carbonate) step.

   A. Using filtration

   B. Using centrifuge

      a. metathesizing both lead and barium with carbonate solution.

      b. metathesizing barium and dissolving the lead with causticized carbonate solution to effect a rough lead removal.

A resin absorption column, full-scale, has been erected in cell #3, Semi-Works, to which is fed the product of step 2Bb above to determine the effectiveness of resin absorption in refining the barium, in lieu of the purification steps (nitric acid and HCl-ether precipitations) now in use. A brief resin absorption process outline follows:

A. Nitric acid slug dissolving.

B. Sulphate Precipitation (using lead carrier).

C. Sulphate Separation.

D. Metathesis, partial lead removal, resolution and made 0.5 <u>M</u> in Ac^-, to column.

E. Caustic elution, removal of lead.

F. pH_3 Citrate elution, removal of iron chronium, nickel.

G. pH_9 Citrate elution, removal of strontium.

H. 6 <u>N</u> HNO_3 elution, barium product.

I. Evaporation to dryness of product and resolution for volume reduction.

Results:

More runs will be necessary before conclusive results are obtained, However, the results below are cited with confidence:

Sulphate Separation		Losses
Filtration (micro-metallic G)	Runs 4 and 5	0.1-0.5%
Centrifugation		
with carrier	Run 9	0.5%
w/o carrier	Run 10	22%
Metathesis		
Filtration		0.1 - 0.2%
Centrifuge		
metathesis only	Run 6	0.3%
metathesis and Pb removal	Run 9	1.5 - 3%
Resin Absorption		
Barium Yield		81%
Loss		1%
Material Balance		82%
Strontium removal		83%
Material Balance		87%

Experimental work will continue to give further information on filter and centrifuge operation, and to refine development of resin absorption process. The latter ultimately will be operated on RaLa plant wastes to demonstrate its ability to function under high radiation intensities.

1. Sulphate Separation

The present RaLa process employs decantation to separate the sulphate precipitate of barium and lead (carrier) from the metal solution. The decantation is mechanically inefficient (losses of 5 - 35%) and time consuming. Both filtration and centrifugation have been tested in the Semi-Works as alternative improvements on the decantation step.

[redacted]

A. Filtration

Filter media were tested to determine the optimum porosity, the greatest capacity consistent with efficient filtration. Micro-metallic stainless media of porosity "G" (4 to 10 micron) was selected and filter was fabricated and installed so that the filter media was suspended by its draw-off line about 1/8 inch above the flat bottom of the precipitation tank. Excellent results were obtained.

Sulphate Separation

Filtration Data

Run	Losses (in hundredths of one percent)					
	Metal solution	Washes				
		1	2	3	4	5
4	2.6	0.7	0.5	0.2	0.21	0.6
5	8.5	0.5	0.2	0.5	0.2	0.5
7*	600	31	15	9	12	
8**	82	0.7	12	0.5	0.4	

Runs 4 and 5 were made according to standard RaLa process conditions. Run 7* was made with uranium solution containing appreciable quantities of graphite which interfered with the filtration by plugging the filter. Back washing frequently to clear the filter probably is responsible for the high losses. In Run 8**, the precipitation was cold, that is, no effort was made to induce "crystal growth" and the higher losses are probably attributable to that departure from the standard process.

[redacted]

B. Centrifugation

The centrifuge data are largely inconclusive because of the many variables that were not closely controlled, feed rate, RPM, however, the results were generally good and the versatibility of the centrifuge recommends it for this service.

Normally lead is added to the dissolver solution to co-precipitate with the barium and carry it down in larger crystals. One run was made without using the carrier, but the loss of barium was too high to justify this short-cut.

Sulphate Separation

Centrifugation Data

Run	Losses in hundredths of one percent					
	Metal Solution	Washes				
		1	2	3	4	5
6*	2120.	320	440	730	350	4
9	8.6	8.3	14.5	9.7	6.2	4.5
10**	1600	80	80	640*		

All of Run #6 and the 3rd wash of run #10 was made with a relatively high and fluctuating feed rate at low centrifuge speed (156 g's). Run #10** was made on barium precipitated without the aid of lead precipitation carrier. Runs 9 and 10 were made at centrifuge speed of 3600 RPM (2500 g's)

2. Metathesis

The metathesis step is required to convert the sulphate precipitate to a carbonate that can be readily dissolved by nitric acid. This is normally done at boiling temperatures to hasten the reaction rate, but cold metathesis were tried and proved successful.

A. Filter

The sulphate crystal apparently breaks up into smaller particles during metathesis and some runs yielded a faintly cloudy filtrate, yet the barium losses were not great.

Metathesis

Filter Data

Run	Losses in hundredths of one percent				
	Metathesis		Washes		
	1	2	1	2	3
4	1.2	0.7	0.6	4	10.5
5	3.6	4.0	2.0	2.2	
7	1.3	75	53		
8	37	24	13	50	

Runs 7 and 8 were metathesized cold (not cooked). Run 4 was made leaving plant-sized heels during filtration and metathesis was incomplete. All other runs were with minimum practical heels and metathesis were exsentially complete.

[redacted]

B. Centrifuge

The metathesis process was varied to use, instead of the usual 3 M carbonate solution, a solution 3 M in OH^- and 0.5 M in $CO_3^{=}$ on the theory that solution of the lead would release "colloidal" crystals of barium which would metathesize more quickly and completely. The dissolved lead was removed with the wash water, effecting a partial removal of the lead carrier.

Metathesis

Centrifuge Data

Run	Losses in hundredths of one percent							
	Metathesis					Washes		
	1	2	3	4	5	1	2	3
6	130	60				2.4	1.2	1.1
9	120	124	21.7	10.4	26.2	14.8	34.4	13.2

About 90% of the lead, calculated on the reduction of the lead to barium ratio, was removed. The relatively high barium losses will probably be reduced when better centrifuge feed controls are devised.

3. Resin Absorption

Experimental equipment of full scale has been installed in cell #3 of the Semi-Works to test the efficiency of resin absorption and selective elution in purifying the barium product. One run only has been made, the product solution contained 81% of the barium from which 83% of the strontium (the most objectionable contaminant) had been removed. As operating experience develops refinements in technique, these results will be substantially improved.

Ultimately, equipment of similar design will be erected near off-gas disposal facilities and a source of 1000 curie levels of barium, and the resin process demonstrated under intense radiation. At the present time, there is no reason for anticipating chemical or mechanical failure of the resin under radiation, but the evaluation of gas formed by the beta-induced dissociation of water may cause 'air-locking' of the column.

[redacted]

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MONTHLY REPORT

Title: Barium 140 Development in the Semi-Works

Work By: I. R. Higgins, R. H. Vaughan, W. A. Horne, R. N. Saleeby, J. B. Goodman, D. B. Masters, W. E. Shockley

SUMMARY

Either a filter or centrifuge has been found to be satisfactory for reducing mechanical losses of lead-barium sulfate and carbonate precipitates which are encountered by decantation in the 706-D equipment. A filter has been recommended for the 706-D equipment change over since it involves less installation expense and is subject to less mechanical failure. Several demonstration filtration runs will be made to verify the low mechanical losses.

The ion exchange development for the final purification of barium is not as complete but to date iron, nickel, chromium strontium and lead separations have been effective with low barium losses in the wastes. Full scale lead removal and sodium removal have not been demonstrated yet. Radiochemical analytical results have been erratic making some difficulty in interpreting operations.

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Results and Discussion

During the period several poor runs have been made for two major reasons (1) incomplete metathesis and (2) graphite in the UNH supplied by Y-12.

(1) Metathesis was incomplete in centrifuge runs 13 and 14 because uranium and sulfate were not completely washed from the Pb-Ba sulfate precipitate. An attempt was made to simplify the procedure for washing precipitates in the centrifuge by displacement of the centrifuge heel liquid by wash liquid as the bowl was running rather than by agitating the bowl slurry with wash liquid and skimming the supernate. From first appearences this was satisfactory but apparently the wash liquid passed thru without mixing with the liquid heel in the bowl.

(2) Three filtration runs 17, 18, and 19 have been slow because of filter plugging. The first filter plugging observed was caused by graphite in Y-12 UNH. When plugging occurred after receiving UNH from which the UNH had been Alsop filtered the plugging was believed to be due to formation of UO_2SO_4 crystals which had been observed once before. However, plugging still occurred when precautions were taken to prevent UO_2SO_4 crystals from forming. Crystals were observed to be absent and graphite to be present on the filter. In another run where extra precautions were taken to remove graphite, filtration was satisfactory i.e, 100 liters filtered in one hour rather than 6 to 24 hours.

A. Filter versus Centrifuge for Separation of Pb-Ba Precipitates

A. Filter

a. No moving parts

b. Low cost installation and maintenance

c. Periodic change necessary because of corrosion or unforseen plugging.

B. B. Centrifuge

a. Subject to mechanical breakdown

b. No periodic change necessary

c. Separation of greater than 95% of the lead is possible with low barium loss

[redacted]

d. Nearly 90% extraction of Ba from 50% UNH solution possible without any Pb carrier.

B. Explanation for the Centrifuge Failure on the Initial Start-up

On several occasions the centrifuge motor current has increased throwing the thermal switch on the control box which, before the motor was rewound with heavier wire, was probably the reason for burning out the motor winding. This period of high motor current was finally observed to occur when the air sparger or sampler was left on the waste tank. The waste tank vent and drain line from the centrifuge are so small that when the sparger is on the air holds the centrifuge liquid from draining into the tank, which means the centrifuge bowl is running in liquid creating the extra drag. Since this discovery it was wondered if the centrifuge motor burned out for this reason when the feed was over 2 liters per minute. A test was made by feeding the centrifuge at 6 liters per minute with the small drain line connected and with it disconnected. Results indicated that the small, 1/4", drain line from the centrifuge rather than a 1/2" or larger was probably the reason for all our centrifuge breakdown.

C. Filtration - Barium Extraction, Metathesis, and Wash Losses

Extraction - 1.13 g $Pb(NO_3)_2$ / Kg UNH
Digestion at 80°-90° 1 hour
Metathesis - 4 M K_2CO_3

Filter - "g" 4 " x 1/16" Micro Metallic

Run	Runs per filter	Extraction	Extraction Washes 1	Extraction Washes 2	Extraction Washes 3	Extraction Washes 4	Extraction Washes 5	Metathesis 1	Metathesis 2	Metathesis Washes 1	Metathesis Washes 2	Metathesis Washes 3
4	1	0.026	0.007	0.005	0.002	0.001	0.006	0.012	0.007	0.006	0.04	0.105
5	2	0.085	0.005	0.002	0.005	0.001	0.005	0.036	0.040	0.020	0.022	—
8	1	0.82**	0.007	0.012	0.005	0.004	—	0.37	0.24	0.13	0.50	—
12	5*	2.85	6.20	3.25	2.41	3.61	4.14	20.90	46.40	2.46	1.32	3.32

* On inspection the filter media was badly corroded and fragile

** $PbSO_4$ precipitation cold with no digestion period

[redacted]

D. Centrifugation - Barium Extraction, Metathesis, and Wash Losses

Extraction 1.13 g $Pb(NO_3)_2$ / Kg UNH
Digestion at 80° - 90° for 1 Hour

Metathesis - 4 M KOH and 0.1 M K_2CO_3

Centrifuge 12" "Bird" - 3600 RPM

Run	Extraction	Losses in Percent Barium											
		Extraction Washes					Metathesis		Metathesis Washes				
		1	2	3	4	5	1	2	1	2	3	4	5
6*	21.2	3.2	4.4	7.3	3.5	0.04	1.3	0.6	2.4	1.2	1.1	0.9	—
9	0.086	0.083	0.145	0.097	0.062	0.045	1.2	1.24	0.217	0.104	0.262	0.148	0.344
10**	16.0	0.8	0.8	—	—	—	—	—	—	—	—	—	—
13	0.84	0.14	0.32	0.18	—	—	1.85	1.50	—	—	—	—	—
14**	12.5	0.06	0.29	0.36	—	—	5.7	—	—	—	—	—	—
15	0.26	0.10	0.03	1.27	0.12	0.13	0.06	1.87	15.0	210	42		
16	20.2	0.09	0.08	0.17	0.25	0.26	6.2	1.48	5.8	0.81	2.05	—	—
17	1.84	—	0.64	0.27	0.45	0.25	—	—	—	—	—	—	—

* At 900 RPM rather than 3600

** With No Pb carrier

[redacted]

E. Filtration - Flow Rates of Extraction and Metathesis Effluents with and Without Graphite Present in the UNH

Vacuum Source - Laboratory Cenco Pump

Graphite 0 - absent
+ - light
++ - medium
+++ - heavy

Filter - 4" in diameter

Run	Graphite	Filter Media	Flow Rate - Liters / Minute	
			Extraction Effluents	Metathesis Effluents
4	0	"G"	1.3 - 1.6	0.2
5	0	"G"	0.5 - 2.0	0.25 - 0.5
7	+++	"G"	Stopped	—
		"F"	Stopped	—
		700-60 screen	0.04 without backwashing to 2.3 with backwashing	—
8	0	"G"	0.7 - 0.9	0.5
11	0	"g"	1.4	—
12*	+	"G"	5.7	> 1.0
17	++	"G"	Start 0.4 - End 0.02	—
18	+	"G"	0.15 - 0.8	0.3
19	++		0.02	—
20	0	G	2.2	—

* Highly corroded filter

[redacted]

[redacted]

F. Total Barium Yields, Losses and Material Balances for all Filtration and Centrifugation Runs with Percent Barium Metathesized Lead Removed

Run	Filter or Centrifuge	Total Losses	Yield	Material Balance	Metathesis Agent	Percent Metathesis	Percent Lead Removal
4	F	0.32	113.0	113.32	~1M K_2CO_3	16.7	—
5	F	0.22	109.0	109.22	~3.5 M K_2CO_3	96.5	—
6	C	47.1	6.0	53.1	3 M KOH 0.5 M K_2CO_3	—	99.3
7	F	9.25	77.0	86.25	3.5 M K_2CO_3	7110	—
8	F	1.89	100.5	102.39	3.5 M K_2CO_3	91.0	—
9	C	4.17	128.1	132.27	3 M KOH 0.5 M K_2CO_3	—	95.4
12	F	96.86	9.55	106.41	4 M K_2CO_3	—	—
14	C	18.9	74.5	93.41	4 M KOH 0.1 M K_2CO_3	poor	—
15	C	271.04	67.2	338.2	4 M KOH 0.1 M K_2CO_3	—	—
16	C	37.39	114.1	151.5	4 M KOH 0.1 M K_2CO_3	—	98.0
17	C	2.40	82.5	84.9	1 M NaAc	5.2	—

Few conditions of the runs are given in Table F but the results are shown to give an idea of the accuracy of the analytical results. Data on the degree of metathesis is meager but on some runs it is known to be very poor either because not enough K_2CO_3 was used, (run 4) or sulfate cake washing was poor (run 14). Na AC did not metethesize Pb SO_4 cake as was observed in run 17. Lead removal was preformed in most centrifugation runs since Ba CO_3 could be positively thrown out from the KOH - K_2CO_3 solution which converted Ba SO_4 to Ba CO_3 and Pb SO_4 to K PBO_2 rather than Pb CO_3. About 95% to 98% Pb removal was accomplished rather than 100% because of the 60% heel left by the centrifuge scoop making a large number of washes necessary. If a centrifuge is used this method of Pb removal is recommended.

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G. Barium Losses, Yields, and Material Balances for the Ion Exchange Procedure

Column - 3" x 3"

Resin - 100 - 200 mesh Dowex 50

Procedure

1. Adsorb metathesized Product
2. Elute Pb with 0.5 NaOH
3. Elute Fe, Ni, Cr with 0.5 M Citric Acid at pH 3
4. Elute Sr with 0.1 M Na Citrate at pH 9
5. Elute Ba with 6 N HNO_3

Run	Barium Losses				Yield	Material Balance
	Feed Waste	Caustic Waste	pH 3 Waste	pH 9 Waste		
Test run	0.71	0.09	0.09	0.11	81.0	81.9
12	0.52	0.01	0.03	2.2	171.0	173.76
13*	36.0	——	7.3	——	70.1	113.4
14*	11.1	——	4.6	11.5	44.9	72.1
15	0.068	0.004	0.24	3.23	64.0	67.54
16	0.006	0.004	0.35	0.19	56.0	56.55

* Runs 13 and 14 were poorly metathesized thus the bulk of the Ba was in the form of sulfate. This explains the heavy column breakthru and high waste losses. It can be observed from table G that barium losses in the wastes are sufficiently low. The reason for the low barium yield for run 15 and 16 is not certain but could be analytical error or channeling in the resin. Observation of elution curves indicates that elutions are complete.

[redacted]

H. Lead, Strontium, Iron, Nickel, and Chromium Decontamination with the Ion Exchange Column

Results are incomplete but in runs 15 and 16 which were centrifugation runs leaving only about 1 gram of Pb, the Pb was reduced to 0.04 g and $<$ 0.03 g respectively in the barium product. Fe, Ni, and Cr analyzed very low and the bulk of the iron was removed either in the Na Ac in the feed or the pH 3 citric acid. The ratio of strontium to barium Beta counts has varied from 0.008, 0.04 to 0.14. In Run 15 about 1/3 of the total Beta counts were reported to be strontium, however, over 200% of the strontium was found in the pH 9 sodium citrate elution indicating that strontium analytical results are possibly in great error. Observation of the elution activity as alwasy shown a very definite and complete elution for strontium.

Future runs on the ion exchange column will be made with full scale amount of lead in the feed.

[redacted]

49-10-260

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FLS-161
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SUMMARY

Little progress has been made during this period because of equipment breakdown and filter plugging. Y-12 supplied UNH has contained sufficient graphite to cut filtration rates through a 4 inch "G" micrometallic filter from 1 to 2 liters per minute to 0.2 liters per minute and less. The graphite has been detected after another Alsop filtration and has been found in the Barium product solutions. All UNH used in the future is to be derived from canned slugs. A 6 inch micrometallic filter is being installed outside the precipitator to simulate the proposed installation in 706-D.

In the ion exchange equipment, 350 ml or 3 inches of resin was not sufficient to give the desired Ba and Sr separation with the full quantity of Pb present, 87 grams. The resin bed has been extended to 7 inches or 800 ml of resin to provide more capacity and more plates for separations. Sodium removal, which has been neglected until now because of corrosion, will be demonstrated on future runs using sulfuric acid rather than hydrochloric.

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